Assessing the Leaching Potential
of
Organic Contaminants In Soils

-A Report Prepared for
Alberta Environmental Protection

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## of
## Organic Contaminants In Soils

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### Alberta Environmental Protection

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# SUMMARY AND RECOMMENDATIONS

1. We have developed relatively simple models for the dissolution of soluble organic carbon in hydrocarbon contaminated soils. The laboratory extraction of soluble organic carbon could be used to determine the total amount and the average partition coefficient of soluble organic carbon in soils.

2. In the six hydrocarbon contaminated soils, target organic compounds, naphthalene, anthracene, phenanthrene, chrysene, benzene, and toluene were detected in extracts where water:soil ratio was as high as 20:1.

3. GC-FID measured total soluble hydrocarbon was not well correlated to the total soluble organic carbon concentration. This may result from the fact that total soluble carbon is a mixture of soluble soil organic matter and hydrocarbons.

4. Soluble organic carbon partition coefficients were weakly correlated with sorption coefficients determined in batch experiments for toluene, anthracene, and naphthalene.

5. Parameters determined in the batch extraction measurements, i.e. the total extractable soluble organic carbon and the average partition coefficient, $K_0$ could be used in the prediction of leaching of soluble organic carbon from soil columns. However, the rate dissolution in the columns is about 100 fold slower than the rate in the batch experiments. Thus, a rate constant appropriate for the particular soil is important for accurate prediction of the leaching of contaminants. However, the flow rate used in the column experiments, i.e. about 0.5 pore volume per hr, could be as much as 100 times or more higher than in the field. The limitation of the rate of contaminant dissolution on the overall transport process increases at the higher flow rates. As the flow rates becomes slow, such as might be expected in the field, a near equilibrium

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condition may exist in which the importance of the rate constant diminishes. Thus, it is concluded that the results of the batch extraction studies could provide a prediction of the upper limit of the overall soluble organic carbon transport in the soils.

6. The average mobility, judged by the equilibrium partition coefficient, of soluble organic carbon in the six hydrocarbon contaminated soils were approximately 5 times higher than the mobility of toluene.

7. Mobility of soluble organic carbon, which could be measured easily, could be used as a screening tool for the assessment of the potential risk of contaminant leaching in the hydrocarbon contaminated soils. There is little risk of contaminant migration in the absence of elevated leaching of soluble organic carbon. Further investigation is needed only if leaching of soluble organic carbon is found to be significant.

8. These conclusions are based on results obtained in laboratory experiments. Their validity under the field conditions remain to be tested.

9. Further study is needed to determine the nature of the soluble organic carbon in the hydrocarbon contaminated soils. Particularly, what proportion of it were of soil organic matter and soil microorganism origin which we are not overly concerned about, and what proportion originates from the contaminants in the soil.

10. In addition, further study is also needed to identify the physical processes responsible for the slow rate constant in soil columns and field soils. Once the processes are identified, prediction of these rate constants from basic physical characteristics of the soil are possible. Only then would it be possible to
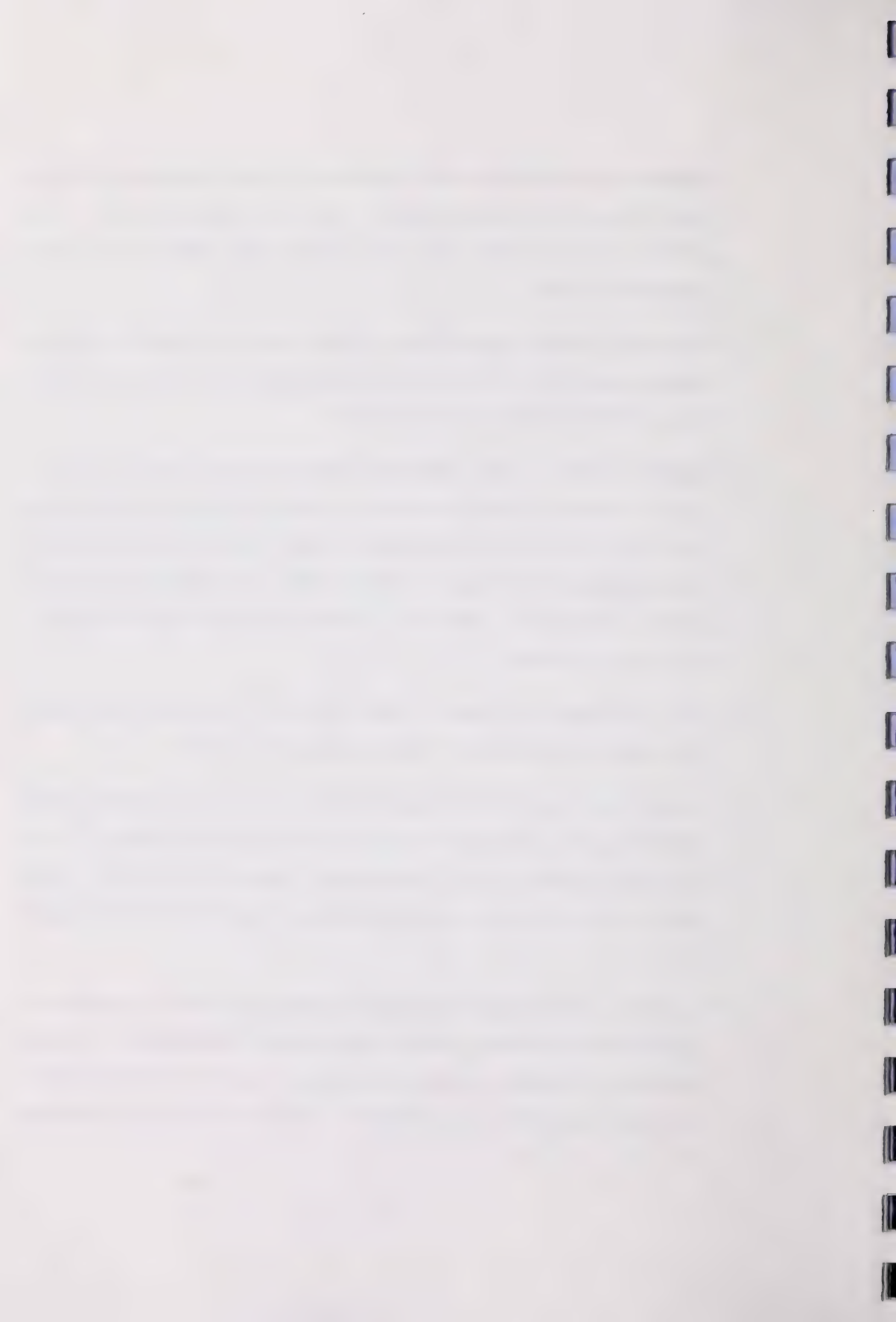
accurately predict the potential of leaching from hydrocarbon contaminanted soils.

## INTRODUCTION

The mobility of organic contaminants in soils is one of the most important factors controlling their fate and movement in the environment. Currently there is a need for a quick, effective, general purpose procedure to provide quantitative assessment of the mobility of organic contaminants in soils, especially when the contamination consists of a mixture of organic chemicals (e.g., hydrocarbons).

The mobility of organic contaminants in soils is inversely related to the extent to which they are adsorbed by the soil matrix (Brusseau and Rao 1989). A chemical that is dissolved in soil water and that does not interact with the soil matrix, is transported through the soil at the average velocity of the water in the soil profile. This is the upper limit of the mobility of any soluble chemical in the soil. Sorption of organic contaminants by soil matrix reduces their mobility through soils. Thus, information on the extent to which a contaminant is adsorbed by the soil matrix is crucial in a quantitative assessment of its mobility through the soil.

Sorption of organic chemicals by soil matrix is largely controlled by the properties of the organic compound, as well as the amount and property of the organic matter in the soil. Empirical relationships have been reported relating sorption behavior of organic compounds in soils to their hydrophobicity (e.g. water solubility, octanol/water partition coefficient) and organic carbon content of the soil (Briggs 1981, Ryan et al. 1988, Webber et al. 1991). These empirical relationships, although useful as an initial screening tool, are of limited value in providing quantitative assessment of contaminant mobility because of their limited accuracy. Soil specific measurements are generally required for the accurate assessment of contaminant mobility through a soil.

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Generally, sorption behavior of organic chemicals in soils is determined by performing batch adsorption studies (e.g. Karikoff 1981, Chiou et al. 1979, McCall et al. 1980) in which various amounts of a specific chemical is added to a soil-water suspension. After sufficient time is allowed for equilibrium, concentration remaining in the liquid phase, after sorption by the soil matrix, is determined. Sorption by the soil is calculated as the difference between amount of chemical initially added and the amount of chemical remaining in the solution after equilibrium. Several measurements with varying initial concentrations of the chemical is needed to determine the sorption isotherm, or the relationship between amount sorbed by the soil and the equilibrium liquid phase concentration.

Several problems are associated with determining the mobility of organic chemicals in soils by this procedure. 1) Approach of equilibrium may require a substantial period (Pignatello 1990, Sawatsky 1995). As a result, these measurements can be time consuming. 2) Sorption behavior of one compound may be influenced by the presence of other compounds (Co-solvents). 3) Laboratory measurements usually measure sorption of freshly added organic compounds whereas desorption of aged contaminants in soils is more important in determining both the environmental fate of the contaminants and the effectiveness of remediation technologies. 4) Contaminated soils often contain a mixture of organic compounds so that the determination of sorption coefficients of even a small fraction of the compounds involved can be difficult.

Extensive literature exists in the use of soil columns to characterize the mobility of organic contaminants through soils (Helling and Dragun 1980, Brusseau and Rao 1989, Jury et al. 1991, Chechai et al. 1993). Sorption coefficient is evaluated on the basis between the relative mobility of a particular compound of concern and water. Helling and Dragun (1980) gave a review of the application of soil column studies for the purpose of assessing contaminant mobility. There are limitations to the general

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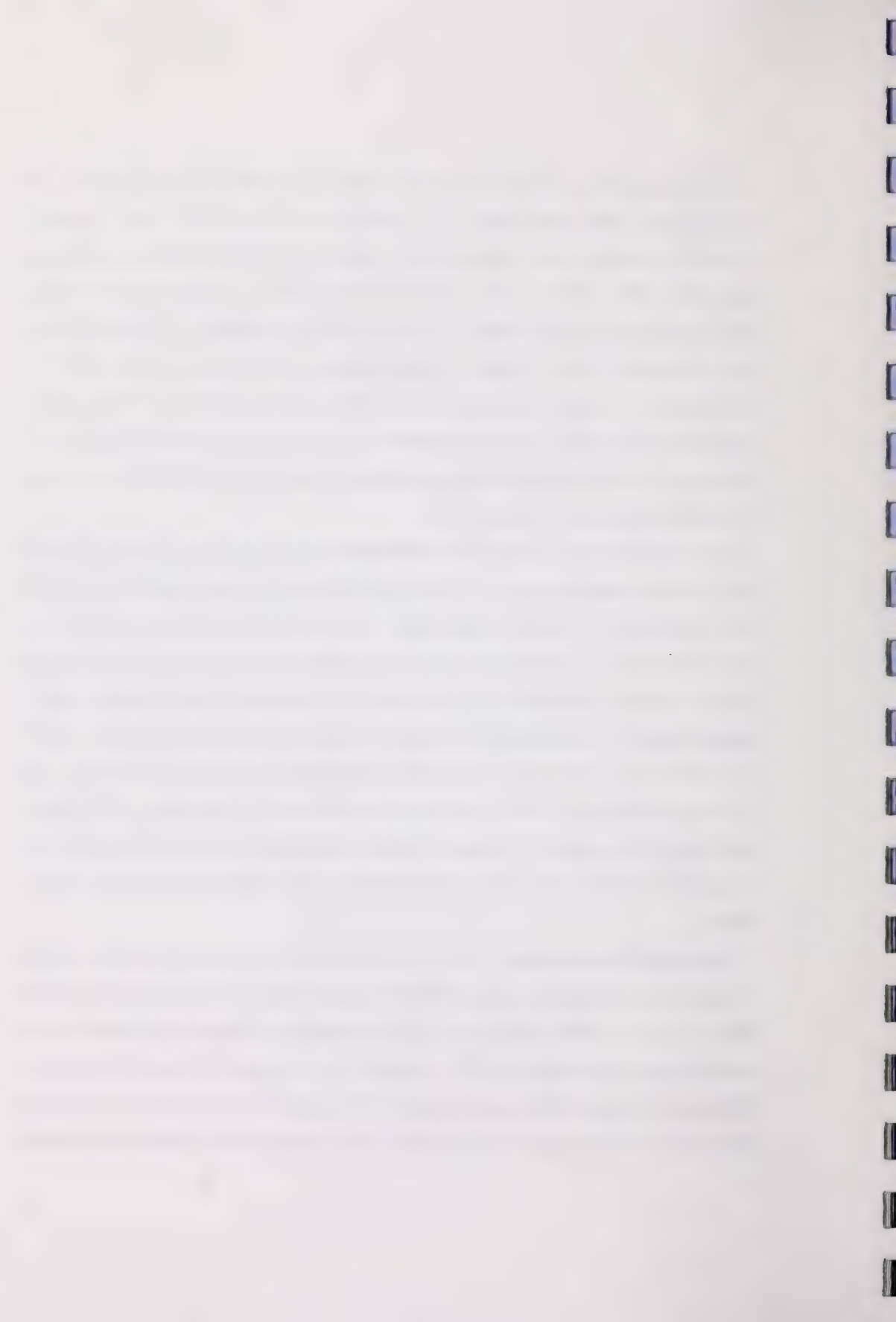
application of the column method in assessing the mobility of organic contaminants in soils, e.g. the measurements are often time consuming; it is difficult to prepare laboratory columns that are truly representative of the field conditions because of spatial and temporal variations in soil properties (Warrick and Nielsen 1980), large number of chemical analysis is required for each soil being tested. Because of the cost and amount of effort involved in soil column measurements, the number of soil samples that must be tested in order to obtain a fair representation of the variability of a specific site may be cost-prohibitive.

Soil thin-layer chromatography has also been used in assessing the mobility of organic chemicals through soils (U.S. EPA 1982, Helling and Dragun 1980). However, the application of this method is limited to the cases where position of contaminants in the soil thin-layer can be easily identified, e.g. radio-isotope labeled compounds.

Simple extraction procedures by water and various chemical agents (e.g. EP-Tox, TCLP, CAM-WET) has also been used to assess leaching potential of contaminants in soils (Dragun et al. 1989, Peralta et al. 1995) in an attempt to separate soil contaminants into fractions associated with the soil material to various degrees. These extraction methods, however, were designed to classify wastes as either hazardous or non-hazardous and generates no information on the mobility of the contaminants (Dragun et al. 1989). The problem associated with these simple extraction procedures is their inability to provide quantitative information on the adsorption of contaminants by the soil matrix, thus is of limited use in assessing the mobility of the contaminants in soils.

There is clearly a need for a quick, inexpensive procedure to screen organic contaminants in soils for their mobility. In this report we show the performance of a simple extraction procedure that can be used to predict mobility of organic contaminants in thesoils based on measurement of soluble organic carbon in soils. Quantitative relation between soluble organic carbon measurments and the sorption coefficients

of the contaminants is also illustrated. Because our methods measures the desorption behavior of contaminants already present in the soil, the information is more relevant for site remediation and risk assessment of existing contaminated sites. The accuracy of the methods are illustrated by comparing predicted and measured soluble organic carbon effluent from soil columns of three hydrocarbon contaminated soils, both before and after bioremediation treatment.

## OBJECTIVES

1. Develop a simple extraction procedure to assess the mobility of organic contaminants in soils.

2. Demonstrate the accuracy of the procedure by laboratory column leaching experiments.

3. Demonstrate the ability of the procedure to predict the mobility of organic contaminants in soils previously contaminated by mixtures of organic chemicals (e.g., hydrocarbons) in laboratory column experiments.

We have selected, particularly to measure the soluble organic carbon in the contaminated soils. Batch extraction studies were used to measure both the quantity of extractable soluble organic carbon in the soils and their average partition coefficients between solid and liquid phases. Sorption coefficients of selected organic compounds of environmental concern were measured and compared to average sorption coefficients of soluble organic carbon in the soils. GC-FID measurements of soluble hydrocarbon in the aqueous extracts were measured to correlate with total soluble organic carbon measurements. GC-MS measurements were performed to identify specific organic compounds of environmental concern in the aqueous soluble organic carbon extracts. Relative mobility of the selected organic compounds in the hydrocarbon

contaminant mixture, as measured by their sorption coefficient, is compared to the average mobility of soluble organic carbon in the soils. By these measurements we show that if there is no risk of significantly elevated leaching of soluble organic carbon from hydrocarbon contaminated soils, the risk of leaching of generally less mobile organic chemicals in the hydrocarbon would not pose a significant environmental risk.

## THEORETICAL CONSIDERATIONS

Several issues must be considered in analyzing sorption and transport of contaminants in soils. In soils containing a complex mixture of contaminants, the first task is to assess the total amount of contaminant easily available for transport. This information can be obtained by analyzing the total water extractable contaminant concentration, e.g. total soluble carbon, and total water extractable hydrocarbon. The second issue is their availability, or the rate of dissolution. The relative rates of dissolution, translocation, and microbial degradation controls the extent of transport of the contaminants. If the rate of dissolution is considerably lower than the potential rate of microbial degradation, there is little risk of extended transport and the subsequent ground water contamination.

### Heterogeneity of hydrocarbon contaminants in soils

We can be certain about two facts concerning hydrocarbon contaminants in soils. Firstly, both the soil and the contaminants are highly complex and heterogeneous. The heterogeneity of soils and contaminants play important roles in the apparent equilibrium distribution and non-equilibrium rate processes of sorption/desorption and the leaching of contaminants. Secondly, our ability to observe and measure the heterogeneity of the complex soil/contaminant system is limited. The question arises naturally as to what can we say about the heterogeneity of the soil system from the

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limited information that can be gathered.

One of the best ways to characterize the heterogeneity of the soil system is statistical distributions of its properties. For example, the heterogeneity of the kinetics of hydrocarbon contaminant desorption can be described by a statistical distribution of its rate constants. However, there will always be uncertainties in our knowledge of the exact distribution function because the information we possess lack sufficient detail and reflect only some gross aspect of the soil system/contaminant system. For example, the apparent dissolution of soil organic carbon may be observed through experimentation. We may be certain that the apparent dissolution reflects the interactions and contributions of all hydrocarbon organic components in the soil. The question is what can we say about the distribution of rate constants and partition coefficients of soil organic components from such observations.

The concept of entropy as a measure of information, or perhaps more appropriately uncertainty or our ignorance of statistical distributions, was first introduced in the pioneering work of Shannon (1948). The maximum entropy principle was first stated explicitly by Jaynes (1957). According to the maximum entropy principle, given some partial information about a quantity characterized by a statistical distribution, the most plausible estimation of the probability distribution function is the one with maximum entropy while being consistent with the information at hand. Since entropy is the description of uncertainty or our ignorance, the maximum entropy principle simply states that aside from what we already know, to be conservative, our best estimate of the statistical distribution is the one that maximizes what we do not know. Kapur (1989) may be referred to for more details in the logic and applications of maximum entropy principle.

The mathematical equaitons describing equilibrium partition of soluble organic carbon in the soils (equation 2) which is used to obtain total extractable soluble organic carbon and their average partition coefficient in the soil, and the equations

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that describes the kinetics of dissolution in the soil (equations 3, 5), which are used to predict leaching of soluble organic carbon cand contaminants from the soil, are all derived based on considerations of the heterogeneity of the soil system by applying the maximum entropy principle.

## Equilibrium Partition

Hydrocarbon contaminated soils contain contaminant compounds with a broad range of properties. Although partition of individual compounds between soil and water has been well understood, the overall dissolution of contaminant mixtures has not been well understood.

Some authors have reported that equilibrium aqueous phase concentrations of PAHs originating from hydrocarbon contaminated soil can be described by Raoult's law. Thus one may write

$$\frac{1}{k} = \frac{c_i^w}{c_i^s - Rc_i^w} \tag{1}$$

where k is the distribution, or sorption coefficient, $c_i^w$ is concentration of $i - th$ component in water, $c_i^s$ is concentration of $i - th$ component in solid phase and $R$ is water/soil ratio of a particular extraction experiment.

Equation 1 applies to partition of a single compound between the aqueous phase and the organic phase. For the partition of a mixtures, such as soluble organic carbon, in soils, we derive our equations based on maximum entropy considerations. Assuming a continuous distribution of the partition coefficient $k$ in the contaminant/soil mixture and that there exists a mean partition coefficient, $K_0$, the equilibrium aqueous phase concentration can be expressed as

$$C_w R = M_s \left(1 + \frac{K_0}{R} e^{K_0/R} \, \text{Ei} \left(-\frac{K_0}{R}\right)\right) \tag{2}$$

where $C_w$ is the total aqueous phase concentration, which could be determined through total soluble carbon concentration, $K_0$ is the average partition coefficient

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and $M_s$ is the total mobile solute concentration in the soil, and $R$ is the water:soil ratio, Ei is the exponential integral function. As $R$ increases, the extraction becomes more complete. Thus, the total extracted soluble carbon, $C_w R$, increases asymptotically and approaches $M_s$ in the limit, as shown in Fig. 1.

One could measure extractable solute concentration at several water:soil ratios and determine the parameters $K_0$ and $M_s$, which can be used to predict the *mean* mobility of soluble organic compounds in the soil.

## Kinetics of organic carbon dissolution

As water moves through the soil, soluble organic compounds are subject to leaching. The amount of mobile organic carbon in the soil represents the total amount of organic compounds that could potentially be leached from the soil. The extent and rate of leaching, however, depends on the rate of dissolution and the rate of water movement. Sorption/desorption processes in soils are often slow. The kinetics of the organic carbon dissolution process must be known in order to accurately predict the leaching process. In an liquid extraction experiment, the concentration of organic carbon in the solution as a function of time and water:soil ration can be expressed, in the Laplace domain, as

$$\bar{C} = \frac{M_s L(s\tau_0)}{s K_0 \left[ R + L(s\tau_0) \right]} \tag{3}$$

where $\tau_0$ is the average rate constant, and $L(s\tau 0)$ is given by

$$L(s\tau_0) = -\frac{1}{s\tau_0} e^{\frac{1}{s\tau}} \, \mathrm{Ei} \left( -\frac{1}{s\tau_0} \right) \tag{4}$$

where Ei is the exponential integral function. Leachate concentration as a function of time can be obtained by numerical inversion of the Laplace transformation function $\bar{C}$.

**Leaching from a soil column**

As water passes a soil column, the aqueous phase concentration in a soil column can be described, in the Laplace domain, by

$$\bar{C} = \frac{M_s}{R + K_0} \left[ \frac{R + K_0 L(s\tau_0)}{s \left[ R + \frac{1}{s}q + K_0 L(s\tau_0) \right]} \right] \tag{5}$$

where $q$ is leaching rate (pore volumes per unit time).

## EXPERIMENTAL METHODOLOGY

**The soils**

Three hydrocarbon contaminated soils, which were previously treated in the solid state bioreactor in a previous study at the Alberta Environmental Center, will be tested.

a. An agricultural top soil contaminated with crude oil and brine (waste I).

b. Diesel invert mud residue (waste II).

c. Flare pit sludge (waste III).

All three wastes were leached to reduce the electrical conductivity of the soil and treated in a bioreactor for at least 1 year prior to land disposal. The contaminated topsoil contained approximately 45,000 mg kg$^{-1}$ TEH hydrocarbon prior to treatment, which was reduced to 20,000 mg kg$^{-1}$ during bioremediation. The diesel invert mud residue and the flare pit sludge initially contained approximately 100,000 mg kg$^{-1}$ TEH. This was reduced to about 9,000 and 30,000 mg kg$^{-1}$ after bioremediation treatment for the diesel invert mud and the flare pit sludge respectively. For all three soils, both the bioremediated and the non-remediated soil were tested.

**Soluble Carbon analysis**

Overall behavior of contaminants were studied by analyzing total soluble carbon concentration in the contaminated soils. The main extraction variable were equilibration time (0.5, 1, 3, 5, 20 hr) and water:soil ratio (5, 10, 20, 100). The measurements with different equilibration times determines overall partition rate and the various water:soil ratios were used to determined the total mobile carbon content in the soil.

The moisture content of the soil samples were determined by drying in an oven at 70C overnight. Water:soil ratios for the extraction experiments were calculated based on soil dry mass, corrected for the water conent of the soils. Triplet samples were used in all measurements. Four different soil:water dilution of 1:5, 1:10, 1:20, and 1:100 is prepared for each soil. For each dilution, specific amount of soil (adjusted for the water content) is weighed carefully and poured into an Erlenmeyer flask, and then water is added according to the desired dilution ratio. The flask is then capped with a stopper wrapped in aluminum foil and put on a shaker (moves about one inch, 170 times per minute) for 0.5 hr, 1 hr, 3 hr, 5 hr, and overnight which is ~20 hr.

After shaking for the desired time, the flask is removed from the shaker and the soil allowed to settled for about five minutes. Then the solutions are transferred to a Teflon centrifuge tube and centrifuged for about 15 minutes at 13,000 r.p.m. The supernatants from the centrifuged tubes are then filtered with 2um glass fiber filter. The clear solution is then analyzed with a automatic soluble carbon analyzer for total soluble carbon concentration.

**GC analysis of soluble hydrocarbon**

For each soil, two soil:water ratios of 1:5 and 1:100 were used. Water extraction of soluble carbon were done as described above. Two extraction times, 0.5 and 20 hrs were used. These measurements were intended to provide the widest ranges in terms

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of extracted hydrocarbon concentrations for correlation with total soluble organic carbon measurements.

Forty (40) ml of water extract was precisely weighed and poured into a 250 ml separator funnel. Thereupon 10 ml methylene chloride (dichloromethane) solution was added to the funnel. The separator funnel with 40 ml soil-water extract and 10 ml methylene chloride was then closed tightly and shaken vigorously for about one minute. After shaking , the separator funnel was placed on a ring holder for about 10 minutes to let the solutions to be separated into two distinct layers. The funnels stopcock was slowly opened and met.chl was collected in an Erlenmeyer flask. Another 10 ml of methalene chloride was added to the funnel and the above procedure was repeated for two more times. Theoretically, in this three collections of met.chl more than 99.9% of the soluble will be transferred from the soil-water extract into the methalene chloride solution. The methalene chloride solution was next taken to a rotaevaporator to be concentrated to about 1.5 ml.

The concentrated solution was next transferred to a small pre-weighed 2 ml vial. The sealed vials were then stored in the refrigerator at 4°C and later analyzed with a Hewlett Packard Gas Chromatograph equipped with a Flame Ionization Detector (GC-FID) for total soluble hydrocarbon.

## GC-MS analysis and hydrocarbon characterization

Soluble carbon extracted with water:soil ration R=5 and 20 were transferred to methylene chloride using liquid-liquid extraction procedure and sent for GC-MS analysis for selected target compounds, i.e. naphthalene, anthracene, phenanthrene, chrysene, benzene, and toluene. The water:soil ratio of 20 was selected after preliminary measurements showed failed to detect consistently all target compounds from extracts at R=100.

Characterization and fractionation of hydrocarbon contaminants in the six waste

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materials were carried out by the Alberta Environmental Center. Asphaltenes were separated by precipitation with pentane. Pentane solubles were fractioned. The fractionation method is based on separation of the hydrocarbon mixture using HPLC techniques. Alkane, PAH, O- and N-PAH, phenol and acid fractions were collected. Identification and quantification of components of each fraction were accomplished by GC-FID and GC-MS techniques.

## Sorption isotherms

Sorption isotherms of the selected target compounds were measured with ^{14}C labeled compounds. Soil solutions were prepared in a 17 ml test tube. Radio labeled compounds of predetermined activity were added to the test tube from a stock solution. The test tubes were then topped with 0.01 M $CaCl_2$ solution, sealed, and placed into an end-to-end agitator for 48 hrs. After equilibration, the soil solution was centrifuged and 5 ml of solution was used in a scintillation counter to determine the solution concentration. An additional 7 ml of solution was also removed. The test tube was then topped with fresh $CaCl_2$ solution, free of labeled compound. The soil was then re-suspended and equilibrated for another 48 hrs. The measurements were repeated for 5 dilution steps for a total reaction time of 240 hr.

## Column study

Columns of 5 cm diameter and 30 cm long for remediated soils and 15 cm long for not remediated soils were used in the studies. The 15 cm column were used for the not remediated soils because consistent flow pattern could not be established on these soils using the longer, 30 cm columns as a result of low hydraulic conductivities of these soils. Because of large number of measurements involved in establishing the break-through curves for each soil column, only total soluble organic carbon concentration

in the effluent were measured. The total soluble organic carbon concentration in the effluent were compared with model predictions, using parameters obtained from batch extraction studies. The purpose of the column experiments were to determine whether the simple extraction procedures could be used to reliably predict solute transport in the soils. Water was pumped though the soil columns at constant flow rates.

## RESULTS AND DISCUSSION

### Soluble Carbon analysis

Results of the soluble carbon analysis are listed in Tables 1–3. Apparent equilibrium was achieved at 20 hr extraction time, based on calculations of the rate constant ($\tau_0 = 1.5$ hr) of the dissolution process in the batch experiments. Equation 2 was fitted to experimental data to obtain total extractable soluble carbon in the soil, $M_s$, and the mean partition coefficient, $K_0$ for the six soils. Results are listed in Table 4. Fig. 2 illustrates the modeled and experimentally measured soluble carbon concentration as a function of water:soil ratio for waste II, not remediated. In this case the parameters are $M_s = 1260$ mg/kg and $K_0 = 9.4$.

Fig. 3 shows the extracted soluble carbon as predicted by equation 2, using the parameters presented in Table 4, compared to measured values at 20 hr extraction. The coefficient of correlation between the two are $R^2 = 0.99$. It should be noted that because the equation 2 has only two parameters, only two measurements could be sufficient to determine these parameters. To test this, $K_0$ and $M_s$ were calculated by fitting equation 2 to only the measured values at R=100 and R=10. The results are not significantly different from those reported in Table 4. Thus we may conclude that to obtain the equilibrium soluble carbon parameters $M_s$ and $K_0$ for the purpose of predicting the potential of leaching of soluble organic compounds from the soil profile,

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a minimum of two extractions are sufficient at R=10 and R=100. However, to guard against unexpected errors, three extractions, at R=10, 100, and a saturated paste extraction would be optimal. Measured values at R=10 and 100 could be used to obtain parameter values for $M_s$ and $K_0$. Equation 2 could then be used to predict the measured soluble carbon concentration of the saturated paste. Agreement between predictions and measurements assures the validity of the model and the calculated parameter values.

It is interesting to notice that for waste II and III, the soluble carbon concentration after remediation is significantly higher than before remediation. At R=5, the soluble carbon concentration for waste II before remediation is 53 mg/kg while after remediation it increased to 65 mg/kg. For waste III, at the same R=5, the soluble carbon concentration increased from 23 to 55 mg/kg after remediation. It is possible that this increased soluble carbon concentration does not represent increased risk of leaching. A significant portion of the increased soluble carbon could be due to increased soil microbial carbon contents after remediation. We do not have data to support this assertion. However, our model analysis, on the other hand, reveals that although higher soluble carbon concentration is observed for waste II and III after remediation, the total extractable soluble organic carbon, $M_s$, in the remediated soils are in fact lower (Table 4). The higher apparent soluble carbon concentration in the remediated soils for waste II and III results from the lower values of the partition coefficient, $K_0$.

In addition to the total amount of extractable soluble carbon that could potentially be leached from the soil profile, knowledge of the rate of desorption/dissolution process is also needed in order to predict the rate of leaching. This information is obtained by comparing soluble carbon concentration at various extraction times. Once the rate of dissolution is obtained, equation 5 can be used to predict leaching of soluble organic compounds from the soil. Equation 3 describes the dissolution of soluble

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organic carbon from soils as a function of time. To test the validity of this equation, the values of $M_s$ and $K_0$ obtained from soluble carbon extraction experiments carried out at 20 hr extraction time were used. The only unknown parameter, the average rate constant, $\tau_0$, is determined by fitting equation 3 to measured soluble carbon concentration at R=10 and t=1 hr. The resulting rate constant $\tau_0$ did not vary significantly between soils. The average value for the rate constant, for the six soils, is $\tau_0 = 1.5 \pm 0.5$ hr. These results, the rate constant, the total extractable soluble carbon content, $M_s$, and the mean partition coefficient, $K_0$, were used in equation 3 to predict soluble carbon concentration at other extraction times, e.g. t=0.5, 1, 3, and 5 hr and at various water:soil ratios. The results are shown in Fig. 4. The correlation coefficient between the predicted values and the measured values are generally $R^2 = 0.98$.

These results suggests that to obtain both the equilibrium ($M_s$ and $K_0$) and kinetic ($\tau_0$) characteristics of soluble carbon dissolution for the batch experiments, it is sufficient to carry out extraction experiments at a few water:soil ratios at t=20 hr, supplemented by extraction at t=1 hr at R=10. In particular, for the extraction at t=20 hr, only three water:soil ratios are necessary, i.e. R=10, 100, and the saturated paste. Omitting the measurements at R=5 does not significantly alter the results of our calculations.

## GC-FID analysis of soluble hydrocarbon

It was hoped that GC-FID analysis of total hydrocarbon in the extract would give us some correlation between total soluble carbon, which is readily measured, and total soluble hydrocarbon. The results of the GC-FID analysis are listed in Table 5.

Although there seems to be an apparent correlation between GC-FID detected water extractable hydrocarbon and total soluble carbon concentration, the correlation is generally poor. The results are shown in Fig. 5.

The apparent reason for the poor correlation is the very high variability between GC-FID determined values. The correlation for individual soils are slightly higher but for each soil the number of points are limited to establish meaningful correlations. One possible explanation for the poor correlation between GC-FID measured soluble hydrocarbon concentration and total soluble carbon concentration is that the total soluble carbon in the soil consists of organic compounds originated from soil organic matter, hydrocarbon contaminants, and soil microorganisms. Thus, soluble hydrocarbon makes up only a part of the total soluble carbon extracted from the soil.

Despite the poor correlation between GC-FID measured soluble hydrocarbon concentrations and total soluble organic carbon content in the soil, one could state that as long as there is no elevated risk of leaching of soluble carbon from contaminated soils, the potential for leaching of hydrocarbon contaminants are minimal. When it is identified that the potential exists for leaching of soluble carbon, further investigation is called for as to the nature of the soluble carbon and whether significant amount of hydrocarbon are contained in the soluble carbon fraction of the contaminated soil.

## GC-MS analysis and hydrocarbon characterization

Characteristics of the hydrocarbon contaminants are shown in Table 6. Bioremediation had little effect on the composition of hydrocarbon in wastes I and III. This has been predicted previously in our modelling study of biodegradation of hydrocarbon contaminants in soils (Feng and Li 1997). The composition of waste II changed significantly after remediation (Table 6). However, this is to be expected since the total hydrocarbon content of this waste material decreased from over 10% to less than 1% after remediation. The change in hydrocarbon composition for waste II, and the lack of change in hydrocarbon composition for wastes I and III are also reflected in the GC-MS spectrums.

One of the objectives of the GC-MS analysis is to confirm whether specific tar-

get compounds, i.e. naphthalene, anthracene, phenanthrene, chrysene, benzene, and toluene are present in appreciable amounts in the soluble carbon fraction. For all six waste materials, all of the target compounds were detected in the soluble carbon fraction, although quantitative determination of concentration was not satisfactory due to high variation. Detectable amounts of benzene and toluene were present in extracts of water:soil ratio, R=100, where total soluble organic carbon concentration in the extract were as low as a few mgs/kg.

These results, although qualitative, confirm the presence of these compounds in the soluble carbon fraction. This supports the assertion that as a first step in a screening process, leaching potential of soluble organic carbon from hydrocarbon contaminated soils can be used to suggest whether further investigation is needed. Where significant leaching of soluble organic carbon is not a problem, the potential for leaching of hydrocarbon would unlikely be a significant risk.

**Sorption isotherms**

Sorption isotherms of selected compounds were determined to show whether the $K_0$, the mean partition coefficient of soluble organic carbon in the soils, and the rate constant, $\tau_0$, of soluble organic carbon dissolution are representative of the target compounds.

Results of the sorption isotherm determinations for naphthalene, anthracene, and toluene are listed in Table 7. In General the Kp values are well correlated with the total hydrocarbon contents of the soils, as shown if Fig. 6 for toluene. It is also seen that the Kp values increases throughout the measurement period. Although at 240 hr, one still could not definitely state that equilibrium has been reached, for all three compounds, most of the sorption occurred within 48, after which sorption increased only slightly. These results are consistent with the soluble carbon extraction results in that they indicate a relatively fast rate constant.

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It is informative to compare PAH Kp values (Table 7) with the mean $K_0$ value of all soluble organic carbon in the soil (Table 4). Although there is indication that the partition coefficient between PAHs and $K_0$ correlated, the correlation coefficients are generally low. Fig. 7 shows the relation between Kp of toluene and $K_0$.

The Kp values for toluene, on average, are 5 times higher than $K_0$. This indicates that the movement of toluene in the soil is slower than the average movement of soluble organic carbon. However, because of the correlation between Kp for toluene and the apparent partition coefficient of soluble organic carbon, $K_0$, total soluble carbon movement would be a good indicator of the fate and transport of toluene in these soils. For naphthalene, the Kp value is generally an order of magnitude higher than that of toluene, or about 50 times of $K_0$. Thus the mobility of the naphthalene, originating from the hydrocarbon contaminants in the soil would be much lower than that of soluble carbon. For anthracene with partition coefficients of more than an order of magnitude higher than naphthalene, there is little chance of it becoming mobile in the soils unless released specifically in preferential flow channels. In these soils because the hydrocarbons has been aged, such likelihood is small.

**Column study**

The effluent concentration as a function of cumulative effluent volume (pore volumes) are for the six soils are shown in Fig. 8-13. The y axis shows the soluble organic carbon concentration in the effluent and the x axis shows the cumulative flux of water that has passed the columns (Q) in units of pore volumes. The mean flow rates for the remediated soils were 5 pore volumes per day and for not remediated soils were 10 pore volumes per day.

For all soils, there is a very high initial concentration which decreases sharply with increasing water cumulative water flux and quickly levels off at low values. These results could not be adequately modeled by either first order, exponential decay or

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the more elaborate convection-dispersion model.

For the not remediated soils, the flow was stopped for approximately 12 hrs (over night) after 9 pore volumes of water has passed through the column. For all three soils, there was an immediate increase in effluent concentration at Q=10. For remediated soils, flow was stopped for 10 days after 19 pore volumes of water has passed through the soil. Increased effluent concentration after the flow was resumed were also apparent for all three soils. However, after the resumption of flow, for both remediated and non remediated soils, the effluent concentration quickly decreased to what would be expected had the flow not been stopped (Fig. 8-13). These results indicates a overall desorption process much slower than the dissolution process observed in the batch experiments.

As stated earlier, the convection-dispersion equation can not be used to adequately describe the effluent concentration change of the column experiments. Equation 5, derived for the case of slow sorption process described by a family of rate constants following maximum entropy distribution, was used to model the effluent concentration from the column experiments. The total extractable soluble organic carbon, $M_s$, and the average partition coefficient of the soluble organic carbon, $K_0$, are equilibrium parameters. The values obtained from batch extraction studies were used in model predictions. Since it is apparent that the desorption rate in the column experiments were much slower than in the batch extraction experiments, the rate constant obtained from the batch experiments could not be used. The faster dissolution rate in the batch experiments is the result of the shaking and abrasion between soil particles and aggregates which are not present in the columns. Thus, rate constant for the model, equation 5 were selected to fit observed effluent concentration at Q=5 pore volumes. The rate constant thus determined were then used, along with $M_s$ and $K_0$ determined in the batch extraction experiments, to predict the effluent concentration for the entire duration of the column experiment. The calculated rated constants for

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the soil columns are listed in Table 4. As discussed earlier, the average rate constant in the batch experiments averaged at 1.5 hr and there is no significant difference between soils. The dissolution process in the columns are in general much slower, with rate constants ranging from $\tau = 17$ hr for remediated waste III to $\tau = 250$ hr for non remediated waste III. For both waste II and III, the dissolution process is much faster for the remediated soil than before remediation. This probably is indicative of the fact that higher fraction of the soluble organic carbon in the soils after remediation are probably soil microbial origin and are more easily available. For waste I, the rate constants are comparable for the remediated and the non remediated soils.

Table 1. Results of soluble carbon analysis for waste I. R is water:soil ratio; t is extraction time; C is soluble carbon concentration, STD is standard deviation; CR is amount of soluble carbon extracted. All concentrations are averages of triplicate measurements.

| Waste 1 not remediated | | | | | Waste 1 remediated | | | | |
|---|---|---|---|---|---|---|---|---|---|
| R | t (hr) | C (ppm) | STD | CR | R | t (hr) | C (ppm) | STD | CR |
| 5 | 0.5 | 118.6 | 4.2 | 593.0 | 5.0 | 0.5 | 31.1 | 4.5 | 155.7 |
| 10 | 0.5 | 35.3 | 2.0 | 353.0 | 10.0 | 0.5 | 25.1 | 2.1 | 251.0 |
| 20 | 0.5 | 25.3 | 3.0 | 505.3 | 20.0 | 0.5 | 14.0 | 0.6 | 280.0 |
| 100 | 0.5 | 6.6 | 0.9 | 660.0 | 100.0 | 0.5 | 4.2 | 0.5 | 423.3 |
| 5 | 1.0 | 102.0 | 8.9 | 510.0 | 5.0 | 1.0 | 47.7 | 1.2 | 238.5 |
| 10 | 1.0 | 47.7 | 0.2 | 477.3 | 10.0 | 1.0 | 26.6 | 1.0 | 266.3 |
| 20 | 1.0 | 27.1 | 0.9 | 541.3 | 20.0 | 1.0 | 14.9 | 0.6 | 298.7 |
| 100 | 1.0 | 7.6 | 0.3 | 760.0 | 100.0 | 1.0 | 4.2 | 0.3 | 416.7 |
| 5 | 3.0 | 110.0 | 3.9 | 550.2 | 5.0 | 3.0 | 54.9 | 0.3 | 274.3 |
| 10 | 3.0 | 54.7 | 1.9 | 546.7 | 10.0 | 3.0 | 29.1 | 0.3 | 290.7 |
| 20 | 3.0 | 32.0 | 2.2 | 640.7 | 20.0 | 3.0 | 16.4 | 0.8 | 328.7 |
| 100 | 3.0 | 7.9 | 0.5 | 793.3 | 100.0 | 3.0 | 4.9 | 0.3 | 486.7 |
| 5 | 5.0 | 103.7 | 13.3 | 518.5 | 5.0 | 5.0 | 55.4 | 0.8 | 277.2 |
| 10 | 5.0 | 55.8 | 4.7 | 558.0 | 10.0 | 5.0 | 33.0 | 0.8 | 330.0 |
| 20 | 5.0 | 32.5 | 1.0 | 650.0 | 20.0 | 5.0 | 17.7 | 0.4 | 353.3 |
| 100 | 5.0 | 8.3 | 0.4 | 833.3 | 100.0 | 5.0 | 5.1 | 0.2 | 506.7 |
| 5 | 20.0 | 142.1 | 3.4 | 710.3 | 5.0 | 20.0 | 49.8 | 2.1 | 249.2 |
| 10 | 20.0 | 68.8 | 3.5 | 687.7 | 10.0 | 20.0 | 33.9 | 0.6 | 338.7 |
| 20 | 20.0 | 39.1 | 1.3 | 782.0 | 20.0 | 20.0 | 22.9 | 1.6 | 458.7 |
| 100 | 20.0 | 10.33 | 0.3 | 1033.3 | 100.0 | 20.0 | 6.1 | 0.3 | 610.0 |

Table 2. Results of soluble carbon analysis for waste II. R is water:soil ratio; t is extraction time; C is soluble carbon concentration, STD is standard deviation; CR is amount of soluble carbon extracted. All concentrations are averages of triplicate measurements.

| Waste 2 not remediated | | | | | Waste 2 remediated | | | | |
|---|---|---|---|---|---|---|---|---|---|
| R | t (hr) | C (ppm) | STD | CR | R | t (hr) | C (ppm) | STD | CR |
| 5 | 0.5 | 32.5 | 4.8 | 162.3 | 5.0 | 0.5 | 46.1 | 7.0 | 230.3 |
| 10 | 0.5 | 25.4 | 0.4 | 254.0 | 10.0 | 0.5 | 32.4 | 1.7 | 324.0 |
| 20 | 0.5 | 16.8 | 1.2 | 335.3 | 20.0 | 0.5 | 19.0 | 0.9 | 379.3 |
| 100 | 0.5 | 7.3 | 1.8 | 726.7 | 100.0 | 0.5 | 6.1 | 0.7 | 610.0 |
| 5 | 1.0 | 49.2 | 1.2 | 246.2 | 5.0 | 1.0 | 68.7 | 0.8 | 343.3 |
| 10 | 1.0 | 29.1 | 2.1 | 290.7 | 10.0 | 1.0 | 32.3 | 1.7 | 323.0 |
| 20 | 1.0 | 16.7 | 1.2 | 333.3 | 20.0 | 1.0 | 20.1 | 1.1 | 402.7 |
| 100 | 1.0 | 7.2 | 0.3 | 716.7 | 100.0 | 1.0 | 7.0 | 0.5 | 696.7 |
| 5 | 3.0 | 52.5 | 0.5 | 262.7 | 5.0 | 3.0 | 77.7 | 1.5 | 388.3 |
| 10 | 3.0 | 30.3 | 1.0 | 303.3 | 10.0 | 3.0 | 39.1 | 4.6 | 391.3 |
| 20 | 3.0 | 19.4 | 0.5 | 388.7 | 20.0 | 3.0 | 23.7 | 2.6 | 474.0 |
| 100 | 3.0 | 7.7 | 0.1 | 773.3 | 100.0 | 3.0 | 7.6 | 1.1 | 760.0 |
| 5 | 5.0 | 57.2 | 1.1 | 285.8 | 5.0 | 5.0 | 82.6 | 1.5 | 413.0 |
| 10 | 5.0 | 32.5 | 0.5 | 325.0 | 10.0 | 5.0 | 44.1 | 1.7 | 441.0 |
| 20 | 5.0 | 20.5 | 0.1 | 410.0 | 20.0 | 5.0 | 26.3 | 0.4 | 526.7 |
| 100 | 5.0 | 8.0 | 1.0 | 800.0 | 100.0 | 5.0 | 7.1 | 0.3 | 710.0 |
| 5 | 20.0 | 53.0 | 1.5 | 264.8 | 5.0 | 20.0 | 65.0 | 1.3 | 325.0 |
| 10 | 20.0 | 32.9 | 0.6 | 328.7 | 10.0 | 20.0 | 47.5 | 3.3 | 475.3 |
| 20 | 20.0 | 21.6 | 0.7 | 431.3 | 20.0 | 20.0 | 30.0 | 0.6 | 600.7 |
| 100 | 20.0 | 8.6 | 0.8 | 863.3 | 100.0 | 20.0 | 8.9 | 0.8 | 893.3 |

Table 3. Results of soluble carbon analysis for waste III. R is water:soil ratio; t is extraction time; C is soluble carbon concentration, STD is standard deviation; CR is amount of soluble carbon extracted. All concentrations are averages of triplicate measurements.

| Waste 3 not remediated | | | | | Waste 3 remediated | | | | |
|---|---|---|---|---|---|---|---|---|---|
| R | t (hr) | C (ppm) | STD | CR | R | t (hr) | C (ppm) | STD | CR |
| 5 | 0.5 | 17.6 | 3.1 | 88.2 | 5.0 | 0.5 | 43.0 | 0.5 | 214.8 |
| 10 | 0.5 | 12.4 | 0.7 | 123.7 | 10.0 | 0.5 | 22.1 | 1.8 | 220.7 |
| 20 | 0.5 | 8.4 | 0.3 | 167.3 | 20.0 | 0.5 | 11.0 | 2.0 | 219.3 |
| 100 | 0.5 | 3.6 | 0.3 | 356.7 | 100.0 | 0.5 | 3.8 | 0.6 | 376.7 |
| 5 | 1.0 | 27.3 | 1.7 | 136.5 | 5.0 | 1.0 | 44.6 | 0.3 | 223.2 |
| 10 | 1.0 | 13.5 | 0.6 | 134.7 | 10.0 | 1.0 | 21.5 | 4.0 | 215.0 |
| 20 | 1.0 | 9.0 | 0.6 | 180.0 | 20.0 | 1.0 | 11.9 | 0.3 | 238.7 |
| 100 | 1.0 | 4.2 | 0.4 | 420.0 | 100.0 | 1.0 | 4.0 | 0.4 | 403.3 |
| 5 | 3.0 | 27.2 | 0.5 | 136.0 | 5.0 | 3.0 | 49.2 | 0.7 | 245.8 |
| 10 | 3.0 | 14.2 | 0.8 | 141.7 | 10.0 | 3.0 | 24.8 | 1.9 | 247.7 |
| 20 | 3.0 | 9.7 | 0.8 | 193.3 | 20.0 | 3.0 | 13.9 | 0.9 | 278.7 |
| 100 | 3.0 | 4.2 | 0.4 | 420.0 | 100.0 | 3.0 | 4.2 | 0.3 | 420.0 |
| 5 | 5.0 | 29.8 | 2.3 | 148.8 | 5.0 | 5.0 | 48.2 | 0.8 | 240.8 |
| 10 | 5.0 | 14.6 | 0.6 | 146.3 | 10.0 | 5.0 | 23.6 | 3.2 | 235.7 |
| 20 | 5.0 | 10.2 | 0.7 | 203.3 | 20.0 | 5.0 | 14.5 | 0.7 | 290.0 |
| 100 | 5.0 | 4.3 | 0.2 | 430.0 | 100.0 | 5.0 | 4.3 | 0.1 | 430.0 |
| 5 | 20.0 | 23.6 | 4.4 | 118.0 | 5.0 | 20.0 | 55.1 | 1.8 | 275.3 |
| 10 | 20.0 | 18.3 | 0.6 | 183.3 | 10.0 | 20.0 | 30.2 | 0.8 | 301.7 |
| 20 | 20.0 | 11.5 | 1.0 | 230.7 | 20.0 | 20.0 | 16.0 | 1.3 | 320.0 |
| 100 | 20.0 | 5.0 | 0.3 | 503.3 | 100.0 | 20.0 | 4.8 | 0.2 | 476.7 |

Table 4. Total extractable soluble carbon (Ms) and mean partition coefficient (K0) of the six soils.

|              | Ms (ppm) | K0  | $\tau$ (hr) |
|--------------|----------|-----|-------------|
| waste I NR   | 1160     | 2.4 | 74          |
| waste I R    | 730      | 3.0 | 110         |
| waste II NR  | 1260     | 9.4 | 210         |
| waste II R   | 1090     | 2.6 | 76          |
| waste III NR | 760      | 7.9 | 250         |
| waste III R  | 540      | 1.7 | 17          |

Table 5. Results of GC-FID measured soluble hydrocarbon contents. Soils 1, 3, 5 and wastes I, II, III, not remediated, respectively. Soils 2, 4, 6 and wastes I, II, and III remediated, respectively.

| sample | soil | R | t | Peak | C (ppm) |
|---|---|---|---|---|---|
| 1 | 2 | 5 | 0.5 | 23512.3 | 31.13 |
| 2 | 2 | 5 | 0.5 | 11057.9 | 31.13 |
| 6 | 2 | 5 | 20 | 18219.9 | 49.83 |
| 8 | 2 | 100 | 0.5 | 2264.6 | 4.23 |
| 9 | 2 | 100 | 0.5 | 7768.3 | 4.23 |
| 11 | 2 | 100 | 20 | 2850.6 | 6.10 |
| 12 | 2 | 100 | 20 | 491.9 | 6.10 |
| | | | | | |
| 14 | 1 | 5 | 0.5 | 25773 | 118.60 |
| 18 | 1 | 5 | 20 | 17599.8 | 142.07 |
| 19 | 1 | 100 | 0.5 | 1000.3 | 6.6 |
| 20 | 1 | 100 | 0.5 | 4199.7 | 6.6 |
| 21 | 1 | 100 | 0.5 | 2830.6 | 6.6 |
| 23 | 1 | 100 | 20 | 12434.4 | 10.33 |
| 24 | 1 | 100 | 20 | 22380.6 | 10.33 |
| | | | | | |
| 25 | 4 | 5 | 0.5 | 3170.4 | 32.47 |
| 26 | 4 | 5 | 0.5 | 6238 | 32.47 |
| 27 | 4 | 5 | 0.5 | 10891.6 | 32.47 |
| 29 | 4 | 5 | 20 | 23802 | 52.97 |
| 30 | 4 | 5 | 20 | 8914.6 | 52.97 |
| 31 | 4 | 100 | 0.5 | 4139.6 | 7.27 |
| 32 | 4 | 100 | 0.5 | 2997.8 | 7.27 |
| 33 | 4 | 100 | 0.5 | 2135.4 | 7.27 |
| 36 | 4 | 100 | 20 | 1731 | 8.63 |
| | | | | | |
| 38 | 3 | 5 | 0.5 | 248741 | 46.07 |
| 39 | 3 | 5 | 0.5 | 261601.6 | 46.07 |
| 41 | 3 | 5 | 20 | 366038 | 65 |
| 43 | 3 | 100 | 0.5 | 153737.8 | 6.1 |
| 44 | 3 | 100 | 0.5 | 144559.4 | 6.1 |
| 45 | 3 | 100 | 0.5 | 144700.4 | 6.1 |
| 47 | 3 | 100 | 20 | 202458.4 | 8.93 |
| 48 | 3 | 100 | 20 | 174291 | 8.93 |

Table 5 (continued). Results of GC-FID measured soluble hydrocarbon contents. Soils 1, 3, 5 and wastes I, II, III, not remediated, respectively. Soils 2, 4, 6 and wastes I, II, and III remediated, respectively .

| sample | soil | R | t | Peak | C (ppm) |
|---|---|---|---|---|---|
| 49 | 6 | 5 | 0.5 | 13941.6 | 17.63 |
| 50 | 6 | 5 | 0.5 | 9955 | 17.63 |
| 55 | 6 | 100 | 0.5 | 3256 | 3.57 |
| 56 | 6 | 100 | 0.5 | 828.4 | 3.57 |
| 57 | 6 | 100 | 0.5 | 3014.8 | 3.57 |
| 59 | 6 | 100 | 20 | 2326 | 5.03 |
| 60 | 6 | 100 | 20 | 2584 | 5.03 |
| 61 | 5 | 5 | 0.5 | 9911.8 | 42.97 |
| 62 | 5 | 5 | 0.5 | 11233 | 42.97 |
| 63 | 5 | 5 | 0.5 | 15494.8 | 42.97 |
| 65 | 5 | 5 | 20 | 10637.8 | 55.07 |
| 66 | 5 | 5 | 20 | 17987.8 | 55.07 |
| 67 | 5 | 100 | 0.5 | 5628.2 | 3.77 |
| 68 | 5 | 100 | 0.5 | 3926.4 | 3.77 |
| 69 | 5 | 100 | 0.5 | 2759.6 | 3.77 |
| 71 | 5 | 100 | 20 | 2583.2 | 4.77 |
| 72 | 5 | 100 | 20 | 3771.8 | 4.77 |

## Table 6. Hydrocarbon characterization of the six waste materials.

| | Wastes | | | | | |
|---|---|---|---|---|---|---|
| | I. NR | I R | II NR | II R | III NR | III R |
| Pentane soluble | 85.1 | 83.8 | 99.4 | 23.9 | 84.8 | 77.8 |
| Pentane insoluble | 14.9 | 16.2 | 0.6 | 76.1 | 16.2 | 22.2 |
| Pentane Soluble fraction | | | | | | |
| N-Alkanes | 8.6 | 5.9 | 29.0 | 3.7 | 17.1 | 9.5 |
| Other hydrocarbons | 49.1 | 47.3 | 60.1 | 72.6 | 63.6 | 57.6 |
| PAH | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Heterocyc. comp. | 10.4 | 9.7 | 0.8 | 0.1 | 7.8 | 5.5 |
| Phenols | 12.3 | 15.6 | 3.2 | 5.3 | 4.8 | 78.1 |
| Acids | 19.5 | 21.5 | 6.8 | 17.9 | 6.8 | 19.0 |
| N-alkane fraction | | | | | | |
| C10-C15 | 0.1 | 0.1 | 53.0 | 2.2 | 1.1 | 0.8 |
| C15-C20 | 9.8 | 8.3 | 42.9 | 60.5 | 19.5 | 10.5 |
| C20-C25 | 31.8 | 30.2 | 4.1 | 35.0 | 24.7 | 19.7 |
| C25-C30 | 22.4 | 22.1 | 0.0 | 2.3 | 24.3 | 26.8 |
| C30+ | 35.9 | 39.3 | 0.0 | 0.0 | 30.5 | 42.2 |

Table 7. Sorption coefficients of naphthalene, anthracene, and toluene in the six waste materials.

| t (hr) | Wastes | | | | | |
|---|---|---|---|---|---|---|
|  | I NR | I R | II NR | II R | III NR | III R |
| **Naphthalene** | | | | | | |
| 48 | 134.2 | 70.9 | 219.9 | 50.7 | 187.6 | 110.8 |
| 96 | 138.6 | 74.8 | 288.8 | 61.5 | 191.3 | 123.5 |
| 144 | 139.8 | 77.9 | 284.8 | 75.1 | 201.1 | 134.3 |
| 192 | 137.2 | 77.7 | 290.4 | 85.3 | 207.4 | 140.9 |
| 240 | 132.3 | 76.3 | 299.3 | 95.2 | 207.2 | 146.9 |
| **Anthracene** | | | | | | |
| 48 | 3351.2 | 1773.5 | 3380.0 | 1743.3 | 4334.3 | 2442.7 |
| 96 | 3711.3 | 2143.3 | 3288.7 | 2489.4 | 5292.1 | 2621.6 |
| 144 | 4000.2 | 2335.0 | 3855.8 | 3176.3 | 5471.5 | 3166.9 |
| 192 | 4052.9 | 2580.7 | 4610.3 | 4285.3 | 6188.8 | 3236.0 |
| 240 | 4015.9 | 2676.8 | 3997.5 | 4774.6 | 6154.9 | 3734.9 |
| **Toluene** | | | | | | |
| 48 | 18.5 | 7.3 | 53.8 | 4.9 | 29.5 | 15.5 |
| 96 | 18.9 | 7.8 | 56.1 | 5.2 | 31.2 | 16.7 |
| 144 | 19.4 | 8.2 | 61.2 | 5.7 | 31.4 | 17.8 |
| 192 | 19.8 | 8.8 | 61.3 | 6.1 | 31.6 | |
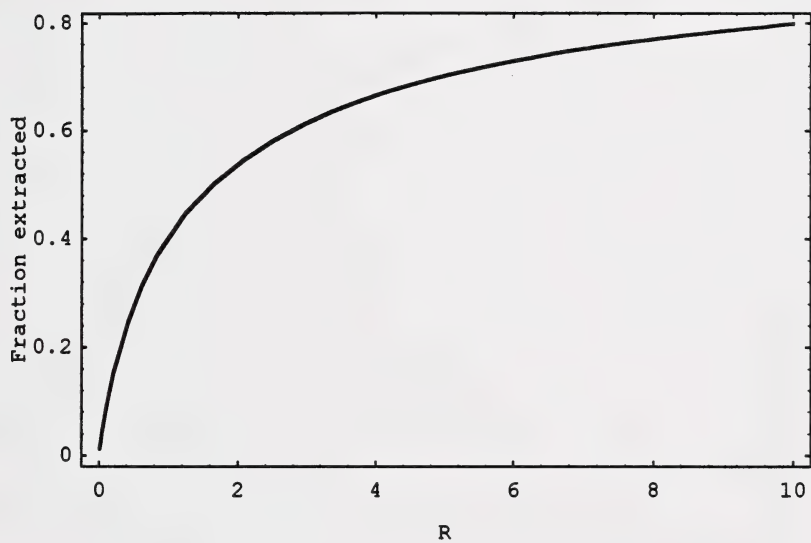
Figure 1. The fraction of total solute carbon extracted, $RC_w/M_s$, as a function of water:soil ratio, R.
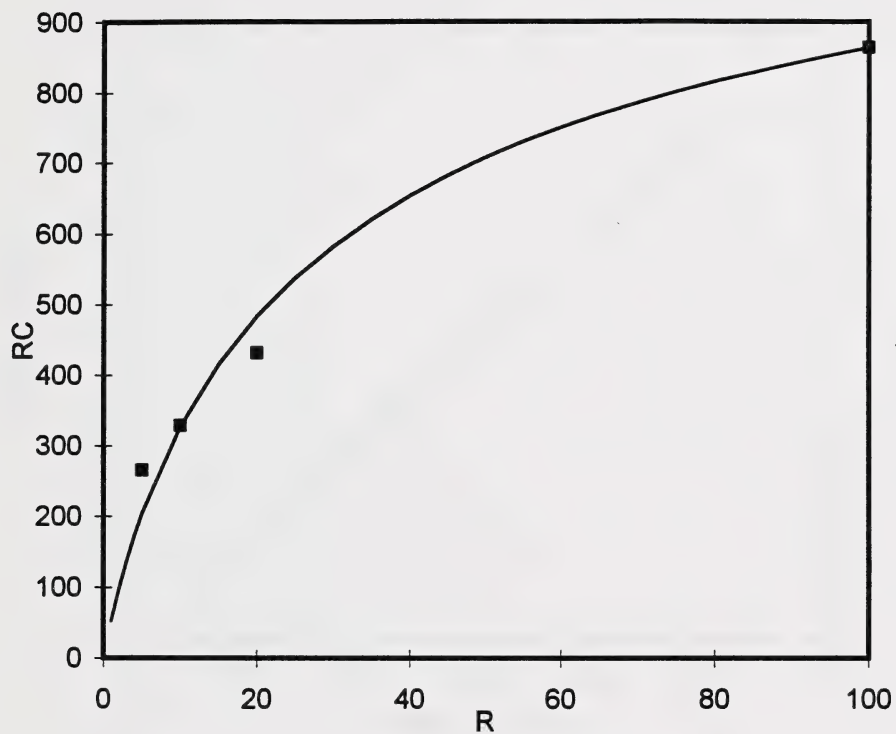
Figure 2. Modeled and measured soluble organic carbon extracted (RC) as a function of water:soil ratio for waste II, not remediated.
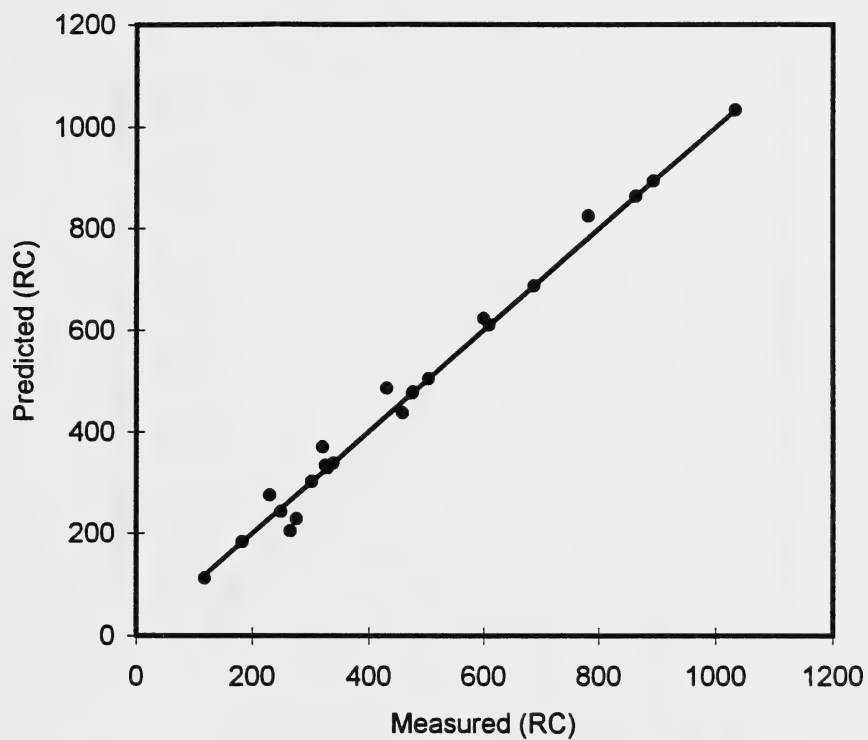
Figure 3. Predicted and measured soluble carbon extracted at apparent equilibrium (t=20 hr) and various water:soil ratios for the six waste materials.
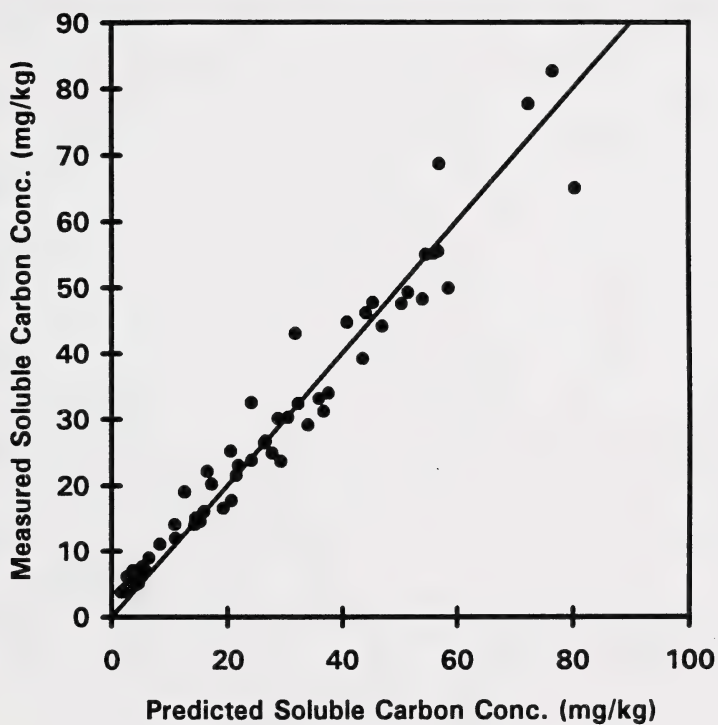
Figure 4. Predicted vs. measured soluble carbon concentration for the six waste materials at various extraction times and water:soil ratios.
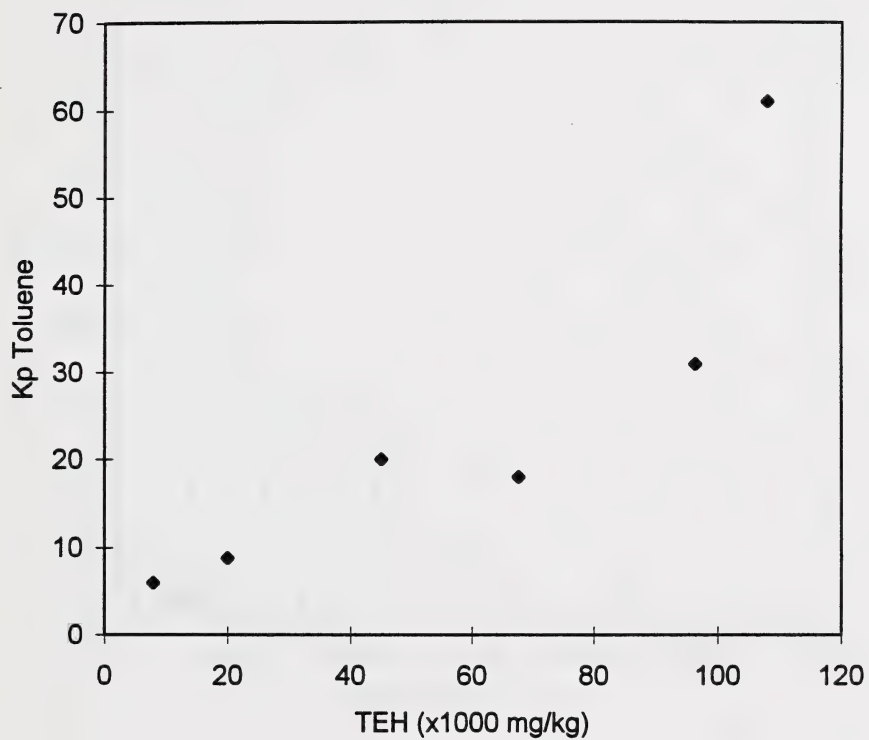
Figure 5. Correlation between GC-FID determined soluble hydrocarbon and total soluble carbon measurements.
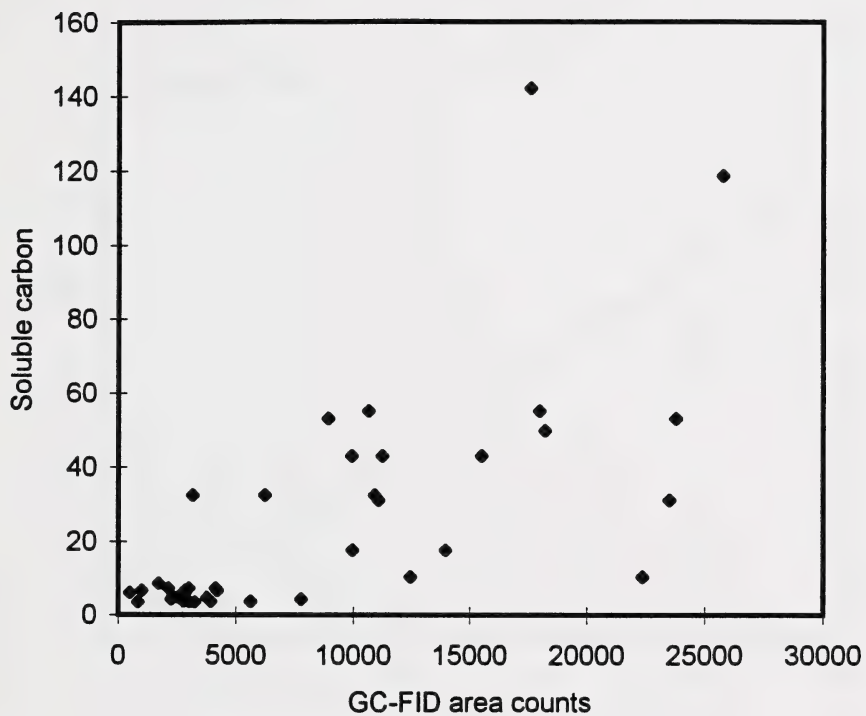
Figure 6. Correlation between Kp for toluene and total extractable hydrocarbon content (TEH).
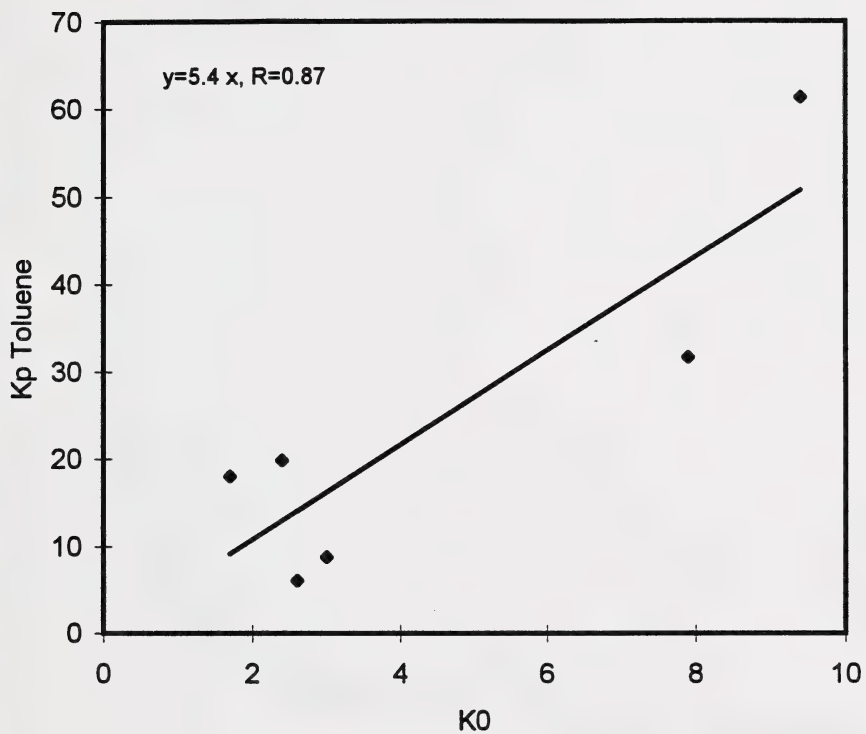
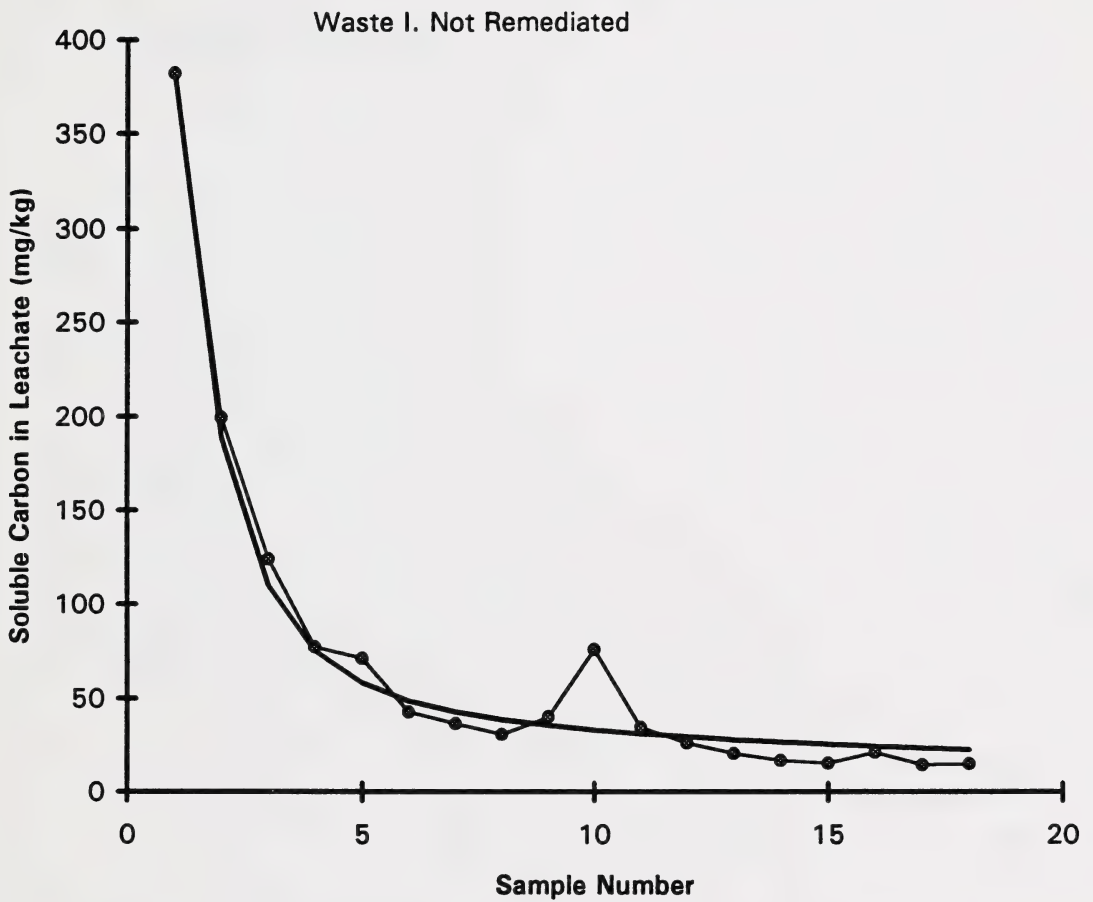Figure 7. Relation between Kp for toluene and the average partition coefficient of soluble organic carbon, $K_0$.

Figure 8. Measured and modeled effluent soluble organic carbon concentration from column experiments for waste I, not remediated.
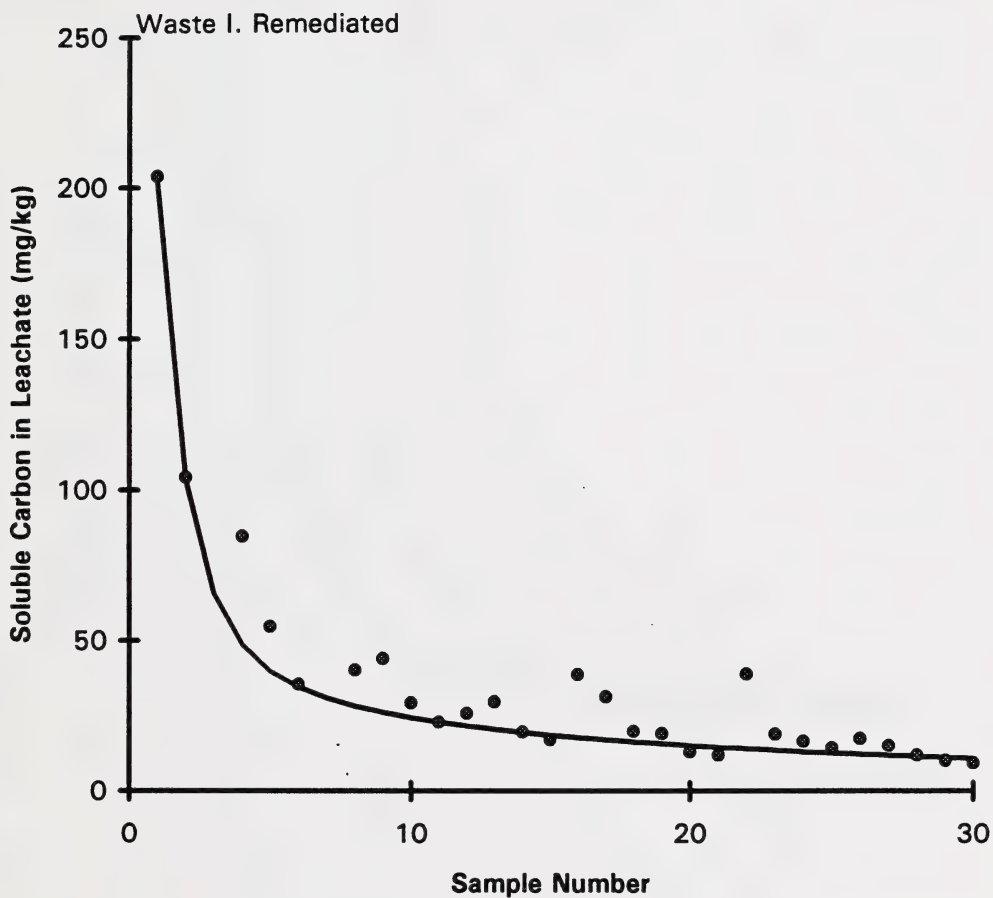
Figure 9. Measured and modeled effluent soluble organic carbon concentration from column experiments for waste I, remediated.
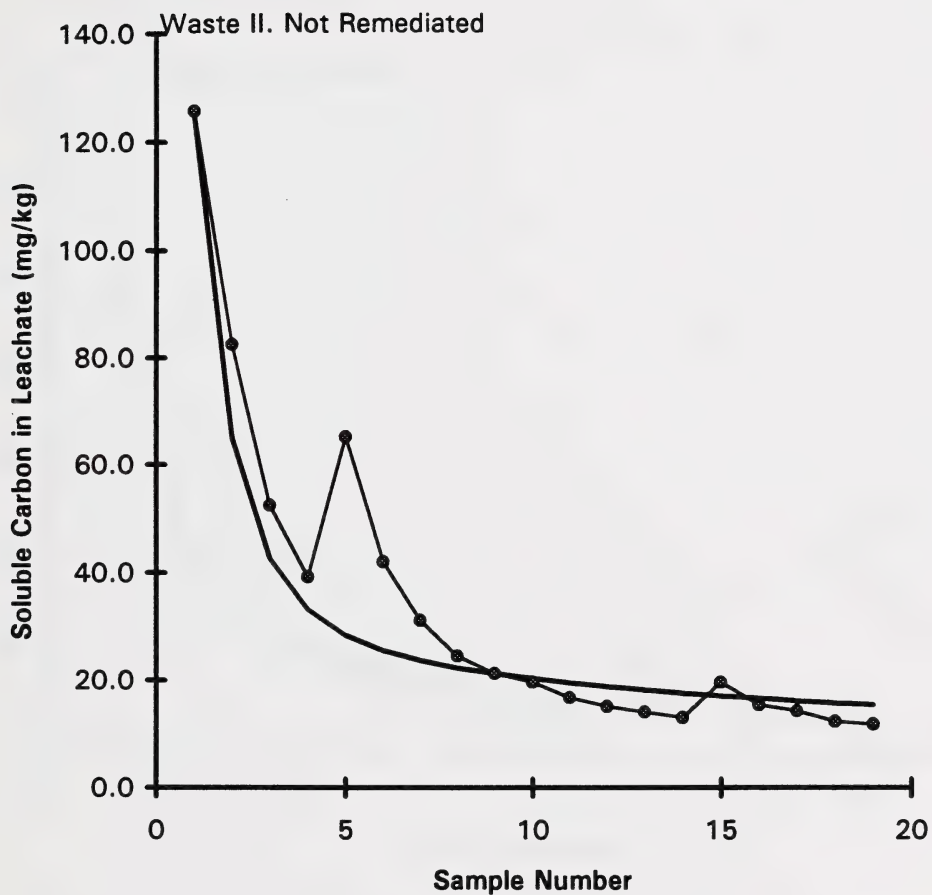
Figure 10. Measured and modeled effluent soluble organic carbon concentration from column experiments for waste II, not remediated.
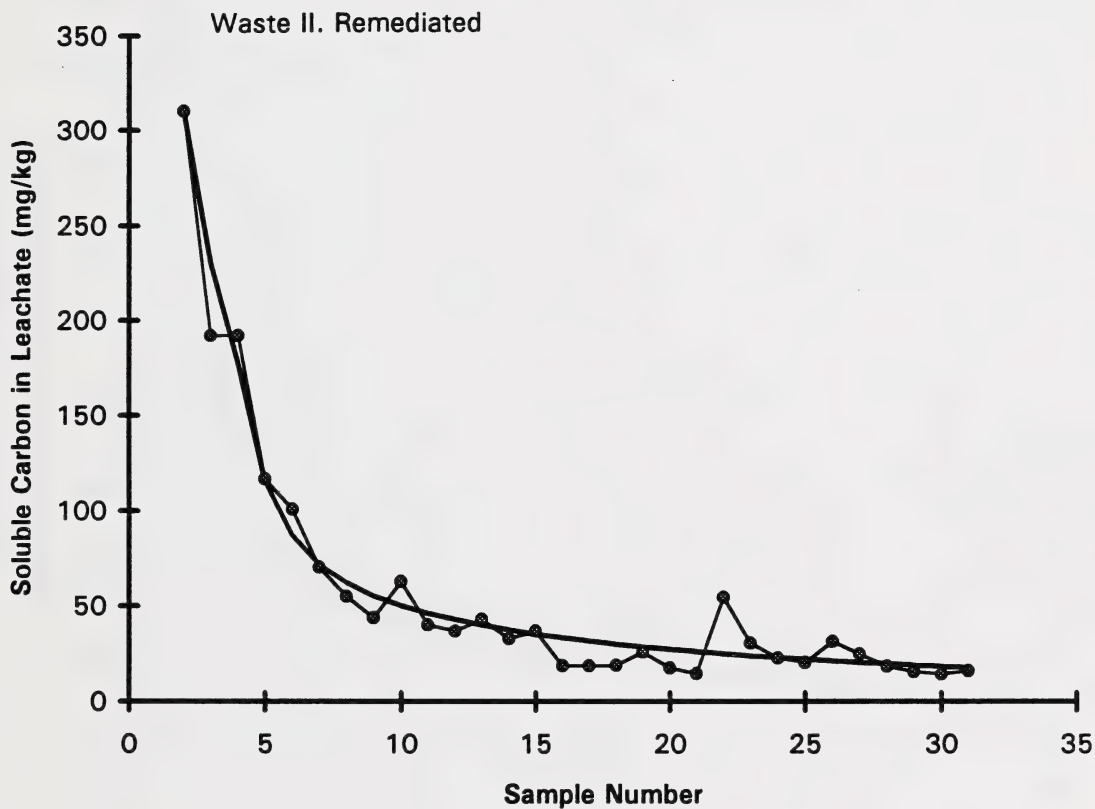
Figure 11. Measured and modeled effluent soluble organic carbon concentration from column experiments for waste II, remediated.
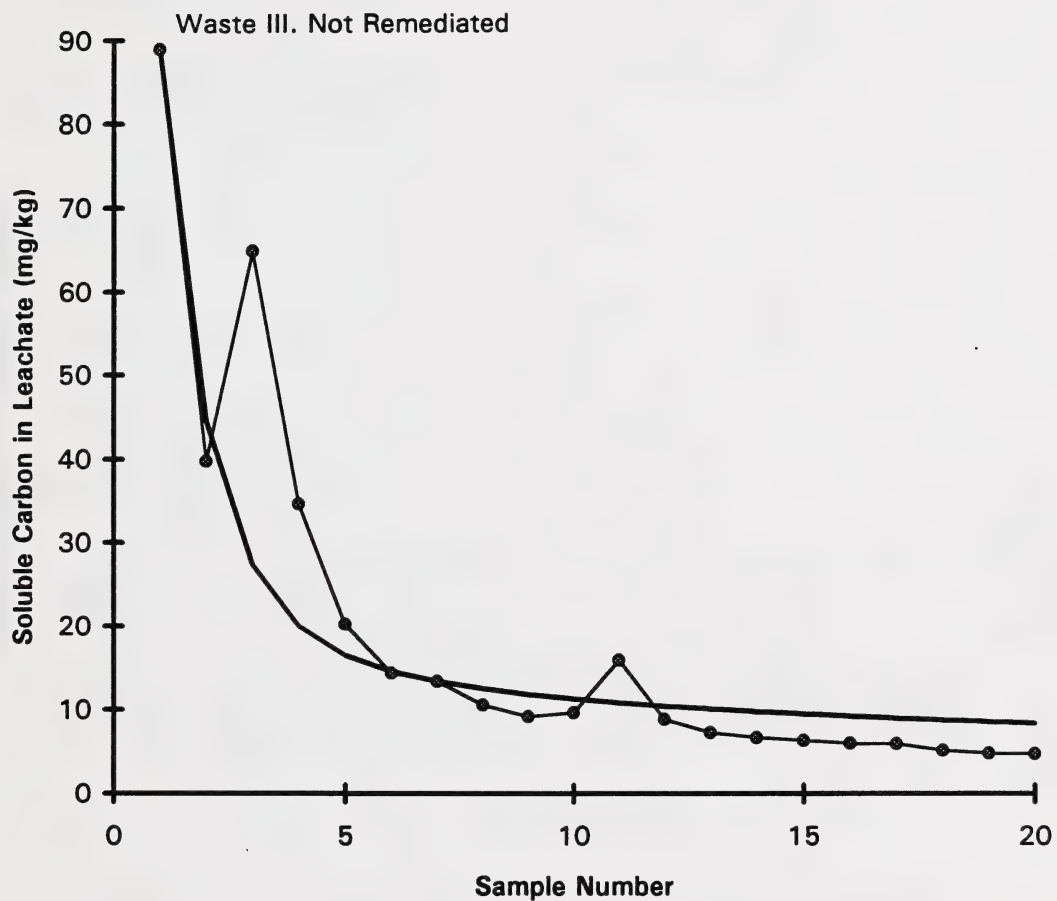
Figure 12. Measured and modeled effluent soluble organic carbon concentration from column experiments for waste III, not remediated.
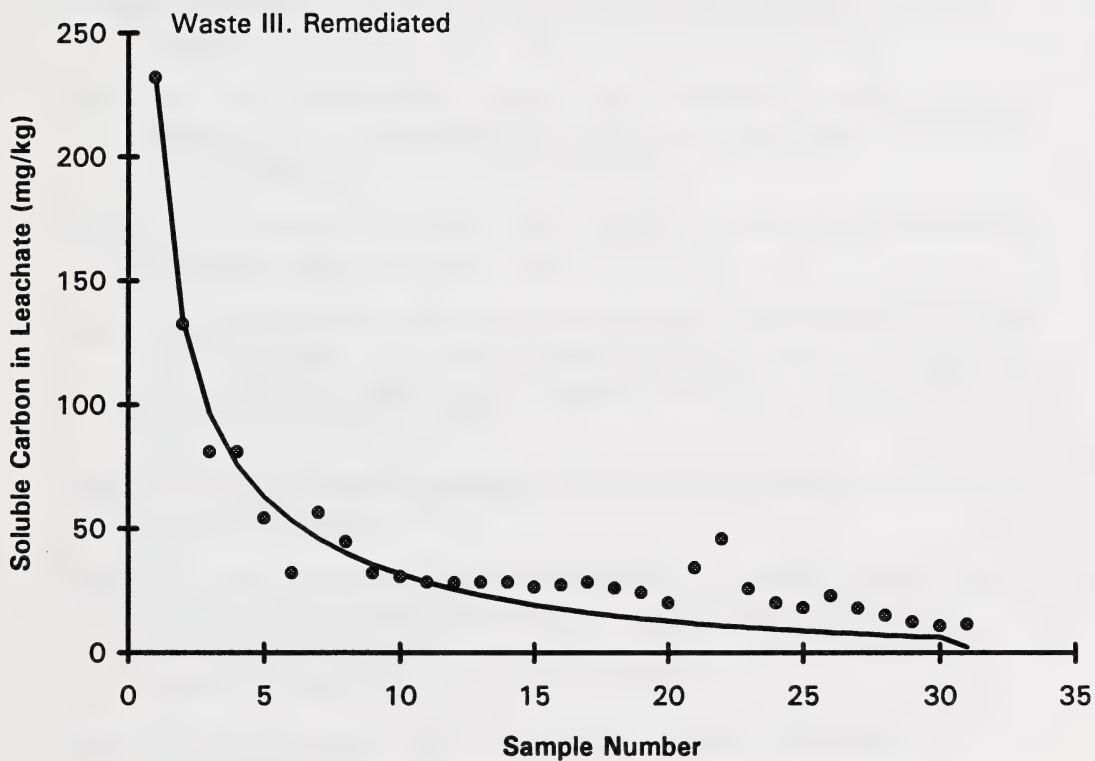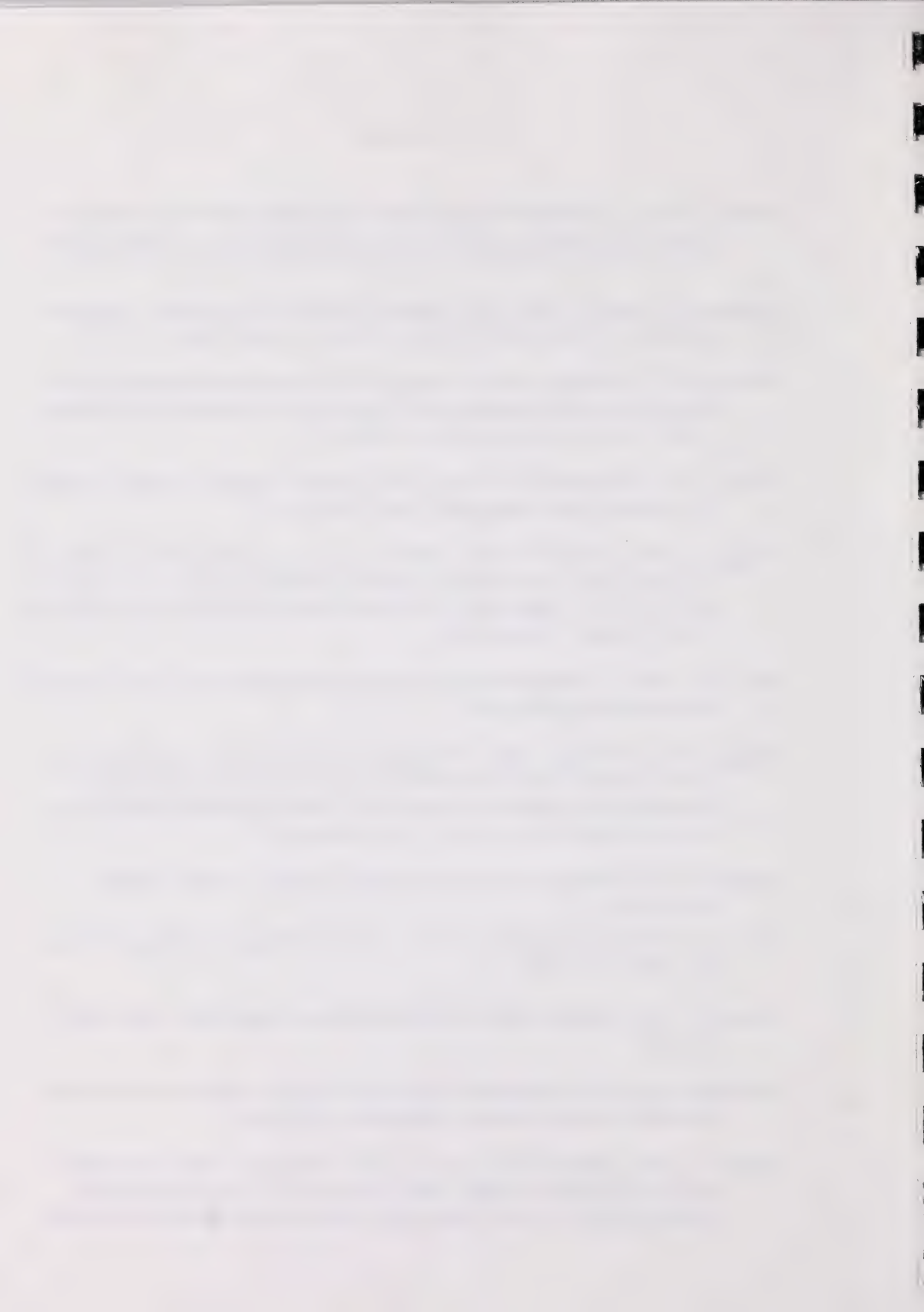
Figure 13. Measured and modeled effluent soluble organic carbon concentration from column experiments for waste III, remediated.

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